Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

p-ISSN: 0972-6268 e-ISSN: 2395-3454	Vol. 16	No. 1	pp. 45-54	2017

Original Research Paper | Open Access

Reactive-Disperse Mixed Dye Wastewater Treatment Using Advanced Oxidation Process

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Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 16-03-2016
Accepted: 16-04-2016

Key Words:
Advanced oxidation
Chelating ligand
Mixed dye wastewater
Transition metal complex

ABSTRACT

This paper studied the efficiency of another series of advanced oxidation processes involving the use of a chelating ligand, combined with a transition metal forming the transition metal complexes to produce reactive radicals. Previous reports using this H_2O_2/pyridine/Cu(II) system focused only on the decolorization of a single synthetic dye wastewater. In practice, real dye wastes contain mixture of dyes. Therefore, in this study, we combined two classes of most widely used dyes namely the reactive dye (RD) and disperse dye (DD) in three different ratios of (RD: DD) = (0.25:0.75), (0.50:0.50), and (0.75:0.25) to obtain a better idea of the trend in the treatment efficiency of this system. Experimental results are assessed in terms of percentage chemical oxygen demand (COD) reduction, decolourisation, and the amount of sludge produced. Optimal concentrations were obtained using statistical design of experiment. At optimal concentrations, for (RD:DD) = (0.25:0.75), (0.50:0.50), and (0.75:0.25), the percentage of COD reduction was recorded at 87%, 86% and 81%, respectively, decolourization at 97%, 98% and 96%, respectively while sludge produced was 185 mg/L, 125 mg/L, and 210 mg/L, respectively.

INTRODUCTION

Wastewater generated from the dyeing and finishing operations of a textile industry is a main source of water pollution considering the effluent composition as well as the volume discharged (Secula et al. 2008). Reactive and disperse dyestuffs are used widely as compared to other dyes due to their superior performance (Kim et al. 2004, Lee et al. 2012, Lee et al. 2014, Lee et al. 2015). Reactive dyes consist of wide ranges of chemical structures and are highly soluble in water making their removal from wastewater difficult by coagulation and activated sludge process (Sermin et al. 2007). Disperse dyes on the other hand caused great environmental concern with their degradation into carcinogenic aromatic amines (Neamtu et al. 2004). Therefore, the treatment of textile wastewater needs to be done to prevent pollution, thereby protecting the environment and public health.

In the past, several treatment methods were applied in the decolourization of this wastewater such as adsorption, coagulation, ozone and hypochlorite oxidations. The practice of these treatment methods is often hindered either by their high operating costs or the secondary pollution that they exhibit (Behnajady et al. 2007). Advanced oxidation (AOP) is another promising treatment method in decolourizing and reducing recalcitrant textile effluent resulting in either the complete mineralization of dyes or the transformation into less complex structures which can be biodegraded easily (Neamtu et al. 2004). AOP is a radical generating system involving the participation of activated oxygen species such as the hydroxyl radicals ($HO^•$), and superoxide anions which can be used in oxidizing a wide range of organic pollutants (Verma et al. 2004a, Baldrian et al. 2006).

The H_2O_2/pyridine/Cu(II) system was developed after it was found that fungi are able to produce a variety of chelating compounds (Watanabe et al. 1998). These compounds, when combined with transition metals, are able to produce radicals in which the radicals were found to be capable in oxidizing a wide range of organic molecules particularly mixtures of complex composition. This system has the advantage of being able to work at a wide range of pH (3-11) as compared to the common Fenton oxidation which works only at acidic conditions pH (2-4) (Baldrian et al. 2006). This system had been investigated in the decolourization of various individual synthetic dyes and the decolourization efficiency of over 90% was reported for most dyes (Nerud et al. 2001, Verma et al. 2004b, Bali & Karagözoglu 2007 a, 2007b).

Based on this information, the aim of this work is to study the capability of this system on the reduction of chemical oxygen demand (COD), the decolourization efficiency as well as the amount of sludge produced at the end of this treatment towards the mixtures of 2 most widely used dyes in 3 different ratios.

MATERIALS AND METHODS

Materials: Experiments were conducted on 1 g/L of synthetic dye mixture comprised of Cibacron Red FN-R (CI Reactive Red 238), a reactive dye (RD) and Terasil Red R (CI Disperse Red 324), a disperse dye (DD). Both dye powders was purchased from CIBA and was used as received without further purification. H_2O_2 (35%) was obtained from R&M chemicals, pyridine from Merck, and $CuSO_4.5H_2O$, NaOH and HCl were obtained from System ChemAR. All chemicals were of analytical reagent grade. Distilled water was used in the preparation of all dye and stock solutions.

Methods: Experiments were conducted using a Jar-Test apparatus (Velp Scientifica JLT 6) which comprised of six stirring rods. Six beakers each filled with 150 mL dye mixture fixed at the initial dye concentration of 1 g/L were used in each run. The ratios of dye mixture in this study were fixed at (RD:DD) = (0.25:0.75), (0.50:0.50), and (0.75:0.25).

The desired pH was adjusted with NaOH or HCl before the addition of H_2O_2, pyridine and $CuSO_4.5H_2O$. Mixing time, mixing speed and reaction time were fixed at 6 min, 60 rpm, and 60 min respectively. All samples were filtered through Sartorius filter paper (pore size 20-25 µm) of which COD, and colour point of the filtrates were determined.

Standard methods was used to determine COD, colour point and total suspended solids (TSS) which measure the amount of sludge produced (APHA et al. 2005).

Statistical Design of Experiment

Full factorial design: Factorial design is useful in the early stages of an experiment and is used widely in the screening of factors (Montgomery 2001). Since previous researchers had reported that pH did not affect decolourization in this system, therefore, percentage decolourization was not included in the factors screening experiment and instead percentage COD reduction was selected as the main response in the screening of factors (Nerud et al. 2001, Verma et al. 2004a, 2004b, Baldarian et al. 2006, Bali & Karagözoglu 2007 a, 2007b). In this system, percentage COD reduction could depend on pH, $[H_2O_2]$, [pyridine] and [Cu(II)]. The effect of these factors and their interactions were measured by performing 3 replicates of 16 experiments to evaluate the standard deviation of each factor, and 2 centre points to detect curvature as given in Table 1. Factor levels were coded as - (low level), 0 (centre point) and + (high level) (Pavan et al. 2007). Concentration of factors used in screening was provided in Table 2. All data analyses were performed using Minitab 14 Statistical software.

Table 1: 2^4 full factorial design.

Experiment	Experimental Factors			
	A	B	C	D
1	-	+	+	-
2	-	+	-	-
3	0	0	0	0
4	-	+	-	+
5	-	-	-	-
6	-	-	+	-
7	+	+	+	-
8	0	0	0	0
9	-	-	-	+
10	-	+	+	+
11	+	-	+	+
12	+	+	+	+
13	+	+	-	+
14	+	-	-	+
15	+	+	-	-
16	+	-	+	-
17	-	-	+	+
18	+	-	-	-

Table 2: Levels of factors for full factorial design.

Factors	Levels	
	−	+
i) (RD:DD) = (0.25:0.75)		
A: pH	4	8
B: $[H_2O_2]$	0.0030 M	0.0050 M
C: [pyridine]	0.0400 M	0.0600 M
D: [Cu (II)]	0.0015 M	0.0017 M
ii) (RD:DD) = (0.50:0.50)		
A: pH	4	8
B: $[H_2O_2]$	0.030 M	0.050 M
C: [pyridine]	0.080 M	0.100 M
D: [Cu (II)]	0.018 M	0.020 M
iii) (RD:DD) = (0.75:0.25)		
A: pH	4	8
B: $[H_2O_2]$	0.010 M	0.030 M
C: [pyridine]	0.040 M	0.060 M
D: [Cu (II)]	0.016 M	0.018 M

Central composite response surface design: Response surface methods are employed to find optimal operating conditions that produced the best response and to model a relationship between factors and the response (APHA et al. 2005). In this study, after performing the screening of factors, a response surface analysis was utilized in order to obtain the highest percentage of COD reduction for all 3 different ratios of dye mixtures. Experiments were carried out according to Table 3 in triplicate. Levels of factors are shown in Table 4.

When a process is relatively close to the optimum, the second order model featuring a curvature is required to ap-

Table 3: Central composite response surface design.

Experiment	Experimental Factors B	C	D
1	+	+	-
2	-	+	-
3	0	0	0
4	+	-	+
5	0	0	0
6	0	0	0
7	+	+	+
8	0	0	0
9	-	+	+
10	-	-	+
11	+	-	-
12	-	-	-
13	0	0	0
14	0	-α	0
15	+α	0	0
16	0	0	+α
17	0	0	-α
18	0	+α	0
19	0	0	0
20	-α	0	0

proximate the response (Montgomery 2001):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1, i<j}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j \qquad ...(1)$$

where, Y is the predicted response, β_0 the offset term, β_i the linear effect, β_{ii} the squared effect and β_{ij} represents the interaction effect. Coded variables were converted to natural variables according to the following relationship (Montgomery 2001).

$$x_k = \frac{\xi_k - x_0}{\delta x} \qquad ...(2)$$

Where, x_k is the coded value of the kth independent variable, ξ_k the natural variable of the kth independent variable, x_0 the natural value of the kth independent variable at the centre point, and δx is the value of step change.

RESULTS AND DISCUSSION

Screening of factors for (RD:DD) = (0.25:0.75), (0.50:0.50), and (0.75:0.25): In this experiment, factors screened include pH, $[H_2O_2]$, [pyridine] and [Cu(II)]. Normal probability plot was used to estimate the effects of factor in which effects that are negligible are distributed normally with mean zero and variance, σ^2 falling on a straight line of this plot whereas significant effects would have non zero means and will not lie along the straight line. The apparently negligible effects are combined as an estimate of error (Montgomery 2001). Fig. 1a, 1b, and 1c showed a normal probability plot of effects for the 2^4 factorial for (RD:DD) = (0.25:0.75), (0.50:0.50), and (0.75:0.25) respectively and the analysis of variance (ANOVA) for (RD:DD) = (0.25:0.75), (RD:DD) = (0.50:0.50), and (0.75:0.25) factors screening is shown in Table 5 (i), (ii), and (iii) respectively. From the ANOVA table, level of significance at 5% probability level was given as values of P less than 0.05.

For (RD:DD) = (0.25:0.75), by examining the normal

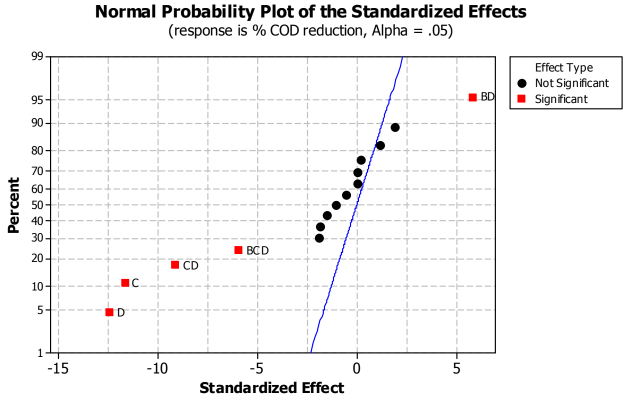

Fig. 1a: (RD:DD) = (0.25:0.75)

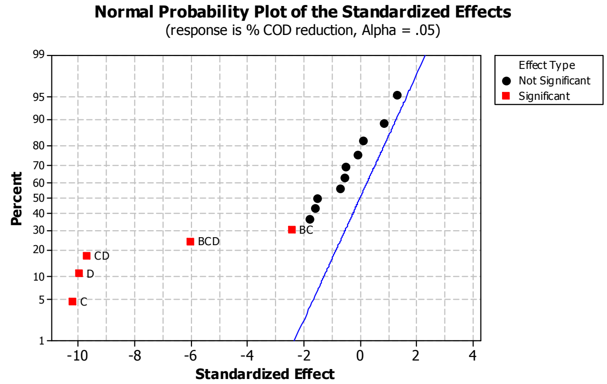

Fig. 1b: (RD:DD) = (0.50:0.50).

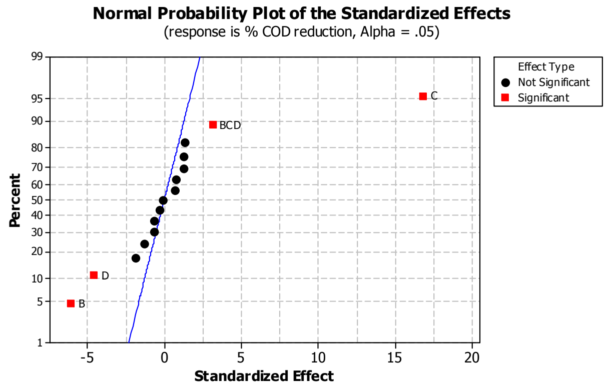

Fig. 1c. (RD:DD) = (0.75:0.25)

Fig. 1: Normal probability plot of effects for the 2^4 factorial.

Table 4: Levels of factors for optimization.

Factors	Levels				
	-α	-	0	+	+α
i) (RD:DD) = (0.25:0.75)					
B: $[H_2O_2]$	0.0020 M	0.0030 M	0.0040 M	0.0050 M	0.0060 M
C: [pyridine]	0.0340 M	0.0400 M	0.0500 M	0.0600 M	0.0660 M
D: [Cu (II)]	0.0014 M	0.0015 M	0.0016 M	0.0017 M	0.0018 M
ii) (RD:DD) = (0.50:0.50)					
B: $[H_2O_2]$	0.024 M	0.030 M	0.040 M	0.050 M	0.056 M
C: [pyridine]	0.074 M	0.080 M	0.090 M	0.100 M	0.106 M
D: [Cu (II)]	0.017 M	0.018 M	0.019 M	0.020 M	0.206 M
iii) (RD:DD) = (0.75:0.25)					
B: $[H_2O_2]$	0.004 M	0.010 M	0.020 M	0.030 M	0.036 M
C: [pyridine]	0.034 M	0.040 M	0.050 M	0.060 M	0.066 M
D: [Cu (II)]	0.015 M	0.016 M	0.017 M	0.018 M	0.019 M

Table 5: ANOVA for factorial design.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
i) (RD:DD) = (0.25:0.75)						
Analysis of variance for COD (coded units)						
Blocks	2	2.040	2.0399	1.0199	3.30	0.049
Main Effects	4	90.249	90.2490	22.5623	72.91	0.000
2-Way Interactions	6	38.697	38.6972	6.4495	20.84	0.000
3-Way Interactions	4	11.944	11.9439	2.9860	9.65	0.000
4-Way Interactions	1	0.333	0.3333	0.3333	1.08	0.306
Curvature	1	11.894	11.8936	11.8936	38.43	0.000
Residual Error	35	10.831	10.8309	0.3095		
Lack of Fit	32	10.450	10.4496	0.3266	2.57	0.238
Pure Error	3	0.381	0.3813	0.1271		
Total	53	165.988				
ii) (RD:DD) = (0.50:0.50)						
Blocks	2	6.852	6.852	3.426	3.35	0.047
Main Effects	4	211.466	211.466	52.866	51.71	0.000
2-Way Interactions	6	106.079	106.079	17.680	17.29	0.000
3-Way Interactions	4	40.049	40.049	10.012	9.79	0.000
4-Way Interactions	1	0.275	0.275	0.275	0.27	0.608
Curvature	1	217.927	217.927	217.927	213.18	0.000
Residual Error	35	35.780	35.780	1.022		
Lack of Fit	32	34.971	34.971	1.093	4.05	0.137
Pure Error	3	0.809	0.809	0.270		
Total	53	618.427				
iii) (RD:DD) = (0.75:0.25)						
Blocks	2	1.431	1.431	0.7153	1.53	0.231
Main Effects	4	160.538	160.538	40.1345	85.88	0.000
2-Way Interactions	6	2.795	2.795	0.4658	1.00	0.443
3-Way Interactions	4	5.112	5.112	1.2781	2.73	0.044
4-Way Interactions	1	0.740	0.740	0.7400	1.58	0.217
Curvature	1	96.296	96.296	96.2956	206.05	0.000
Residual Error	35	16.357	16.357	0.4673		
Lack of Fit	32	13.126	13.126	0.4102	0.38	0.933
Pure Error	3	3.230	3.230	1.0768		
Total	53	283.268				

probability plot in Fig 1a, we conclude that factors D, and C, and the interactions between CD, BCD and BD are significant. From the ANOVA in Table 5 (i), probability results (value) showed that the curvature (= 0.000), are highly significant at a 5% probability level (< 0.05). This suggests that a curvature of factors were detected when the levels changed from low level (–) to high level (+) passing through the centre point (0).

For (RD:DD) = (0.50:0.50), normal probability plot in Fig 1b showed that factors D and C and the interactions between CD, BCD and BD are significant. The ANOVA in Table 5 (ii) suggests that there was a curvature (= 0.000) when the levels changed.

For (RD:DD) = (0.75:0.25), the normal probability plot in Fig 1c showed that individual factors C, B and D, and the interactions between BCD are important. ANOVA in Table 5 (iii) suggests that a curvature (= 0.000) was detected when the levels were changed indicating that operating levels were near optimum.

From this factors screening, we conclude that the individual effect of A (pH) and its interaction with B, C, and D ([H_2O_2], [pyridine] and [Cu(II)]) was not significant in the percentage COD reduction of all 3 mixtures.

According to Robbins and Drago, only few transition metal complexes can catalyse H_2O_2 oxidation above pH 8 (Robbins et al. 1997). However, some chelating ligands were reported to be able to stabilize metal ions even in basic solutions and thus, prevent precipitation (Verma et al. 2004b). In this experiment, the presence of pyridine as the chelating ligand prevented precipitation thus, allowing oxidation reactions to be carried out unaffected at wide pH ranges. Therefore, pH was not evaluated further in this study and following experiments were conducted using the initial pH of the dye mixtures.

Optimization of percentage COD reduction of (RD:DD) = (0.25:0.75), (0.50:0.50), and (0.75:0.25) using H_2O_2/pyridine/Cu II) System: After performing factors screening experiment, a central composite response surface design containing 20 experiments (8 cube points, 4 centre points in cube, 6 axial points and 2 centre points in axial) was carried out according to Table 3 in triplicate in order to obtain the highest percentage of COD reduction. Since a curvature was detected, therefore the second-order model from Eq. 1 was used to model the relationship between the response and the factors (Montgomery 2001). The response surface regression for percentage COD reduction for (RD:DD) = (0.25:0.75), (RD:DD) = (0.50:0.50), and (0.75:0.25) is presented in Table 6 (i), (ii), and (iii) respectively.

For (RD:DD) = (0.25:0.75), the quadratic regression model for the percentage COD reduction in terms of coded factors regardless of their significance is given in Eq. 3:

$$Y = 83.43 - 0.28x_1 - 0.17x_2 + 0.55x_3 + 0.12x_1^2 - 0.01x_2^2 - 0.08x_3^2 + 0.02x_1x_2 - 0.25x_1x_3 + 0.25x_2x_3 \quad ...(3)$$

For (RD:DD) = (0.50:0.50), the quadratic regression model for the percentage COD reduction in terms of coded factors regardless of their significance is given in Eq. 4:

$$Y = 82.45 - 0.34x_1 + 0.76x_2 + 0.18x_3 - 0.01x_1^2 - 0.27x_2^2 - 0.33x_3^2 - 0.34x_1x_2 + 0.14x_1x_3 - 0.07x_2x_3 \quad ...(4)$$

For (RD:DD) = (0.75:0.25), the quadratic regression model for the percentage COD reduction in terms of coded factors regardless of their significance is given in Eq. 5:

$$Y = 76.95 - 1.55x_1 + 1.07x_2 + 0.24x_3 - 0.13x_1^2 - 0.32x_2^2 + 0.19x_3^2 + 0.79x_1x_2 - 0.45x_1x_3 + 0.14x_2x_3 \quad ...(5)$$

where Y is the predicted response (percentage COD reduction) x_1, x_2 and x_3 are the coded values of the respective treatment system factors: H_2O_2, pyridine and Cu(II).

The 3D graphical surface representing models from all 3 Eqs. were generated from Minitab 14 in which Fig. 2a, b and c representing Eq. 3, Fig 3a, b and c representing Eq. 4, and Fig. 4a, b and c representing Eq. 5.

Fig. 2 shows the effect of [H_2O_2], [pyridine] and [Cu(II)] in a response surface plot for the percentage COD reduction of (RD:DD) = (0.25:0.75) dye mixture. From Fig 2a, an increase in both [H_2O_2], and [pyridine] led to a decrease in the percentage COD reduction. Fig 2b showed that the increase in [Cu(II)] increased the percentage COD reduction while increase in [H_2O_2] decreases the COD reduction. It can be seen from Fig. 2c that increase in [Cu(II)] increases COD reduction while increase in [pyridine] decreases the COD reduction. The optimal concentrations resulting in the highest COD reduction was 0.002 M H_2O_2, 0.066 M pyridine, and 0.0018 M Cu(II) with a predicted COD reduction of 85.85% at these combinations.

Fig. 3 shows the effect of [H_2O_2], [pyridine] and [Cu (II)] in a response surface plot for the percentage COD reduction of (RD:DD) = (0.50:0.50) dye mixture. From Fig 3a, increase in [H_2O_2] decreases COD reduction while increase in [pyridine] increases COD reduction. Fig 3b showed that the increase in [Cu(II)] increased COD reduction while increase in [H_2O_2] decreases the COD reduction. Fig. 2c showed that increase in [Cu(II)] and [pyridine] increases the COD reduction. The optimal concentrations were found at 0.024 M H_2O_2, 0.074 M pyridine, 0.0187 M Cu(II) with a predicted

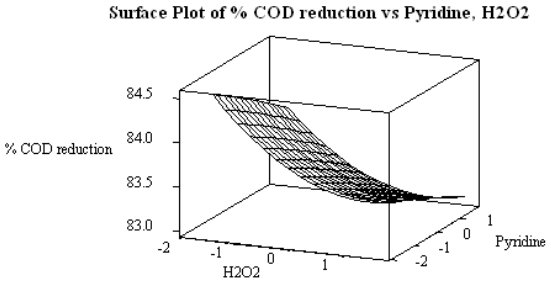

Fig. 2a: Surface plot of $[H_2O_2]$ and [pyridine] towards % COD reduction.

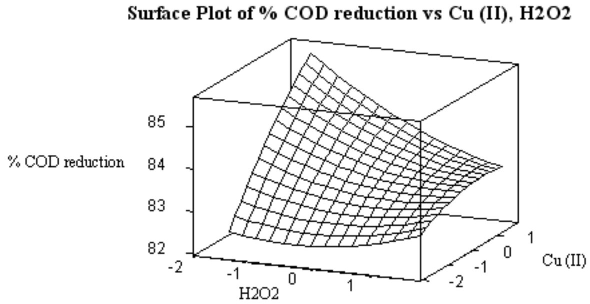

Fig. 2b: Surface plot of $[H_2O_2]$, and [Cu (II)] towards % COD reduction.

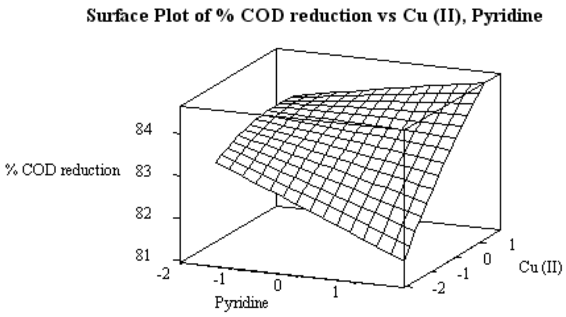

Fig. 2c: Surface plot of [pyridine], and [Cu(II)] towards % COD reduction.

Fig. 2: Surface plot of effects for (RD:DD) = (0.25:0.75) towards % COD reduction.

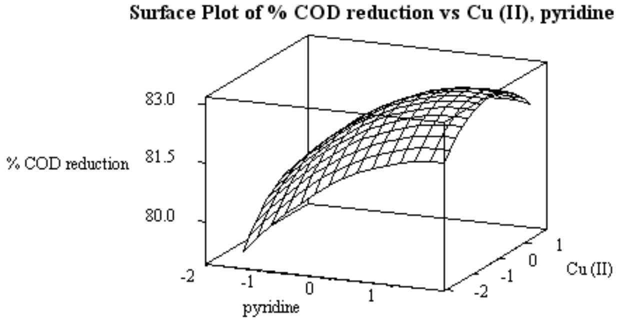

Fig. 3a: Surface plot of $[H_2O_2]$, and [pyridine] towards % COD reduction.

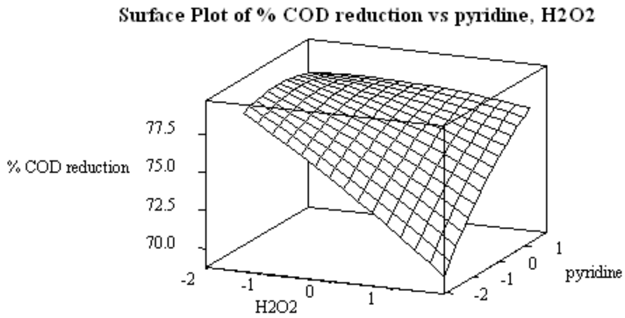

Fig. 3b: Surface plot of $[H_2O_2]$, and [Cu (II)] towards % COD reduction.

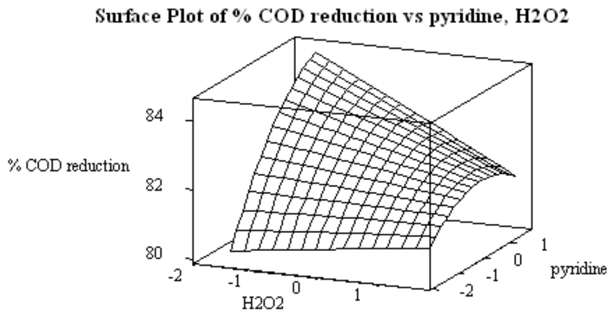

Fig. 3c: Surface plot of [pyridine], and [Cu (II)] towards % COD reduction.

Fig. 3: Surface plot of effects for (RD:DD) = (0.50:0.50) towards % COD reduction.

COD reduction of 84.43%.

Fig. 4 shows the effect of $[H_2O_2]$, [pyridine] and [Cu (II)] in a response surface plot for the percentage COD reduction of (RD:DD) = (0.75:0.25) dye mixture. The same trend as in Fig. 3 was reported in Fig. 4 when the levels of $[H_2O_2]$, [pyridine] and [Cu(II)] were changed. The optimal concentrations were found at 0.004 M H_2O_2, 0.050 M pyridine, 0.0186 M Cu(II) with a predicted COD reduction of 81.19%.

Based on Fig. 2, Fig. 3 and Fig. 4, it was found that higher $[H_2O_2]$ decreases COD reduction though the addition of H_2O_2 was supposed to increased the formation of $^{\bullet}OH$ and thus increase the degradation of dye compound contributing to the reduction of COD. However, was a powerful $^{\bullet}OH$ scavenger. At high concentration, the hydroperoxyl radicals ($HO_2^{\bullet}$) were formed due to excessive H_2O_2 as shown in Eq. 6 and Eq. 7.

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad ...(6)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \quad ...(7)$$

Table 6: Response Surface Regression for percentage COD reduction using H_2O_2/pyridine/Cu(II).

Term	Coef	SE Coef	T	P
i) (RD:DD) = (0.25:0.75)				
Constant	83.4316	0.03532	2362.375	0.000
Block 1	0.1754	0.04036	4.346	0.000
Block 2	-1.1425	0.04743	-24.087	0.000
Block 3	-0.0412	0.04036	-1.022	0.312
Block 4	0.4962	0.04743	10.462	0.000
Block 5	0.2246	0.04036	5.564	0.000
H_2O_2	-0.2759	0.02363	-11.672	0.000
Pyridine	-0.1662	0.02363	-7.032	0.000
Cu(II)	0.5475	0.02363	23.165	0.000
H_2O_2*H_2O_2	0.1186	0.02375	4.992	0.000
Pyridine*Pyridine	-0.0064	0.02375	-0.271	0.787
Cu(II)*Cu(II)	-0.0827	0.02375	-3.482	0.001
H2O2*Pyridine	0.0208	0.03051	0.683	0.498
H2O2*Cu(II)	-0.2450	0.03051	-8.030	0.000
Pyridine*Cu(II)	0.2492	0.03051	8.166	0.000
S = 0.1495 R-Sq = 97.1% R-Sq(adj) = 96.2%				
ii) (RD:DD) = (0.50:0.50)				
Constant	82.4532	0.06670	1236.102	0.000
Block 1	0.5606	0.07624	7.354	0.000
Block 2	1.1994	0.08959	13.388	0.000
Block 3	-1.5410	0.07624	-20.214	0.000
Block 4	-0.5231	0.08959	-5.839	0.000
Block 5	0.1073	0.07624	1.407	0.166
H_2O_2	-0.3439	0.04464	-7.704	0.000
pyridine	0.7577	0.04464	16.973	0.000
Cu(II)	0.1773	0.04464	3.971	0.000
H_2O_2*H_2O_2	-0.0088	0.04485	-0.196	0.845
pyridine*pyridine	-0.2738	0.04485	-6.104	0.000
Cu(II)*Cu(II)	-0.3344	0.04485	-7.456	0.000
H2O2*pyridine	-0.3412	0.05763	-5.921	0.000
H2O2*Cu(II)	0.1429	0.05763	2.480	0.017
pyridine*Cu(II)	-0.0662	0.05763	-1.150	0.256
S = 0.2823 R-Sq = 96.0% R-Sq(adj) = 94.7%				
iii) (RD:DD) = (0.75:0.25)				
Constant	76.9486	0.12532	614.029	0.000
Block 1	0.0209	0.14323	0.146	0.885
Block 2	-0.1637	0.16831	-0.972	0.336
Block 3	-0.0116	0.14323	-0.081	0.936
Block 4	-0.2099	0.16831	-1.247	0.219
Block 5	0.2042	0.14323	1.426	0.161
H_2O_2	-1.5545	0.08386	-18.536	0.000
Pyridine	1.0673	0.08386	12.727	0.000
Cu(II)	0.2443	0.08386	2.913	0.006
H_2O_2*H_2O_2	-0.1321	0.08427	-1.567	0.124
Pyridine*Pyridine	-0.3214	0.08427	-3.815	0.000
Cu(II)*Cu(II)	0.1892	0.08427	2.245	0.030
H2O2*Pyridine	0.7921	0.10827	7.316	0.000
H2O2*Cu(II)	-0.4479	0.10827	-4.137	0.000
Pyridine*Cu(II)	0.1363	0.10827	1.258	0.215
S = 0.5304 R-Sq = 93.2% R-Sq (adj) = 91.0%				

*Analysis was done using coded units.

Though $HO_2^{\bullet}$ is an oxidant, but its oxidation potential is lower and less reactive as compared to $^{\bullet}OH$ and therefore do not degrade any organic substances (Fathima et al. 2008).

Fig. 2, Fig. 3, and Fig. 4 also showed that increase in [Cu (II)] increased COD reduction. This was because the addition of Cu(II) as catalyst had accelerated the degradation of

Table 7: Local solutions for response optimization.

Combination	$[H_2O_2]$	Concentration [pyridine]	[Cu(II)]	% COD reduction (Predicted Value)
i) (RD:DD) = (0.25:0.75)				
1	0.006 M	0.035 M	0.0015 M	83.65 %
2	0.0053 M	0.037 M	0.0016 M	83.46 %
3	0.051 M	0.066 M	0.0018 M	84.12 %
4	0.002 M	0.034 M	0.0018 M	85.18 %
5 (optimal)	0.002 M	0.066 M	0.0018 M	85.85 %
ii) (RD:DD) = (0.50:0.50)				
1	0.056 M	0.092 M	0.0206 M	81.66 %
2	0.056 M	0.087 M	0.0199 M	81.89 %
3	0.043 M	0.091 M	0.0189 M	82.40 %
4	0.024 M	0.080 M	0.0190 M	81.43 %
5 (optimal)	0.024 M	0.074 M	0.0187 M	84.43 %
iii) (RD: DD) = (0.75: 0.25)				
1	0.036 M	0.066 M	0.015 M	77.99 %
2	0.022 M	0.060 M	0.019 M	78.48 %
3	0.004 M	0.036 M	0.019 M	80.57 %
4	0.004 M	0.004 M	0.0186 M	81.07 %
5 (optimal)	0.004 M	0.050 M	0.0186 M	81.19 %

H_2O_2 to $^{\bullet}OH$ which had high oxidation potential of 2.8 eV (Fathima et al. 2008).

Pyridine acts as the chelating ligand in this system (Bali & Karagözoglu 2007b). Pyridine in combination with Cu (II) formed the transition metal-ligand complexes that could decompose H_2O_2 to produced $^{\bullet}OH$ (Verma et al. 2004b). Fig. 2 revealed that COD reduction decreases with the increase of [pyridine] while Fig. 3 and Fig. 4 showed the opposite. This could be due to the ratio of the dye powders used. Fig. 2 showed the surface plots based on (RD:DD) = (0.25:0.75) while Fig. 3, and Fig. 4 showed the surface plots based on (RD:DD) = (0.50:0.50) and (RD:DD) = (0.75:0.25) respectively. This meant that higher [pyridine] would result in higher COD reduction in dye mixtures containing higher reactive dye (RD) while high [pyridine] would result in lower COD reduction in dye mixture with low reactive dye (RD).

COD reduction, colour removal and sludge production of (RD:DD) = (0.25:0.75), (0.50:0.50), and (0.75:0.25) using H_2O_2/pyridine/Cu(II) system: The COD reduction, colour removal and sludge production of the 3 different ratios of dye mixtures using H_2O_2/pyridine/Cu(II) system was provided in Fig. 5a, Fig. 5b, and Fig. 5c respectively. Each of the concentration combinations for each ratio was obtained from a set of solutions generated by Minitab, response optimizer as provided in Table 7 and percentage COD reduction was based on the average of 3 experimentally observed value. The fifth combination is the optimal concentrations in each ratio.

From Fig. 5a, we can conclude that COD reduction was higher when the dye solutions contained higher amount of disperse dyes. For (RD:DD) = (0.25:0.75), the percentage COD reduction was in the range from 84% to 87% and the optimal COD reduction was 87%. For (RD:DD) = (0.50:0.50), the percentage COD reduction was in the range of 85% to 86% and the optimal COD reduction was 86%. Percentage COD reduction ranged from 77% to 81% for (RD:DD) = (0.75:0.25) in which the optimal COD reduction was 81%.

The decolourization of dye wastewater was reported to take place within 30 minutes of reaction time for all oxidation processes (Bali & Karagözoglu 2007b). However, the measurement of colour alone as reported by most papers was insufficient to draw conclusion on the efficiency of a treatment system as the oxidation of structured dye molecules would result in the production of small, colourless organic molecules such as aldehydes, ketones and acetic acids where these molecules in turn increased the concentration of COD (Lin & Lin 1993). Therefore, in this study percentage COD reduction was chosen as the main response in our optimization study.

Fig. 5b shows the percentage decolourization for the 3 different ratios of dye mixtures. For (RD:DD) = (0.25:0.75), the percentage decolourization was in the range of 95% to 97%, for (RD:DD) = (0.50:0.50) from 97% to 98% and for (RD:DD) = (0.75:0.25), percentage decolourization ranged from 96% to 97%. These results proved that this system had high decolourization efficiency.

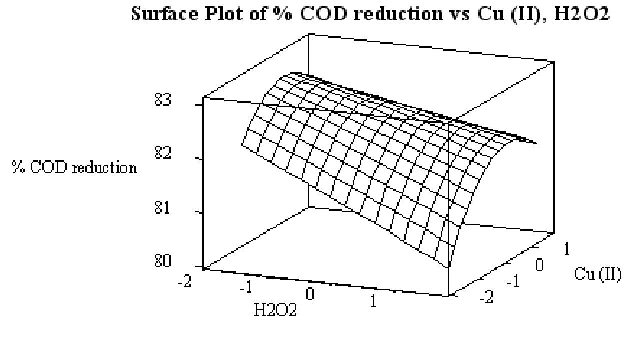

Fig. 4a: Surface plot of [H_2O_2], and [pyridine] towards % COD reduction.

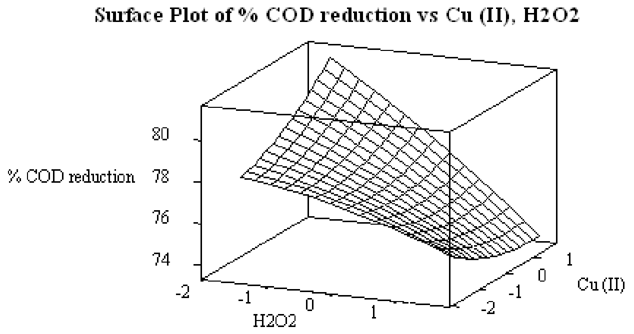

Fig. 4b: Surface plot of [H_2O_2], and [Cu (II)] towards % COD reduction.

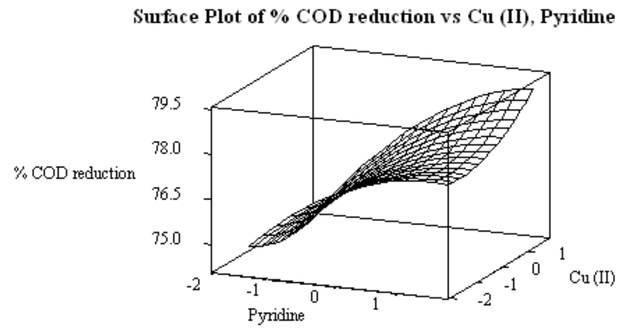

Fig. 4c: Surface plot of [pyridine], and [Cu (II)] towards % COD reduction.

Fig. 4: Surface plot of effects for (RD: DD) = (0.75: 0.25) towards % COD reduction.

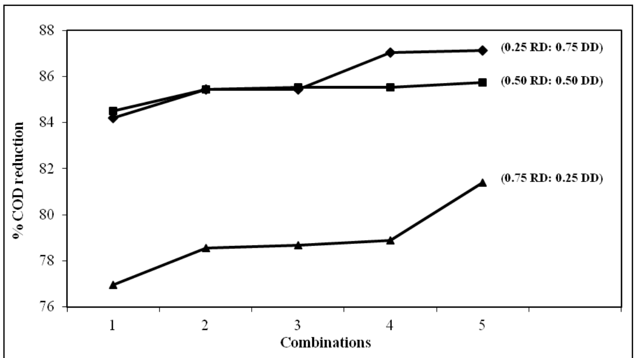

Fig. 5a: Percentage COD reduction.

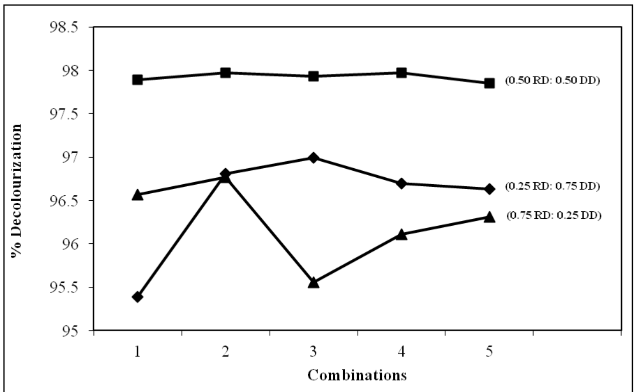

Fig. 5b: Percentage decolourization.

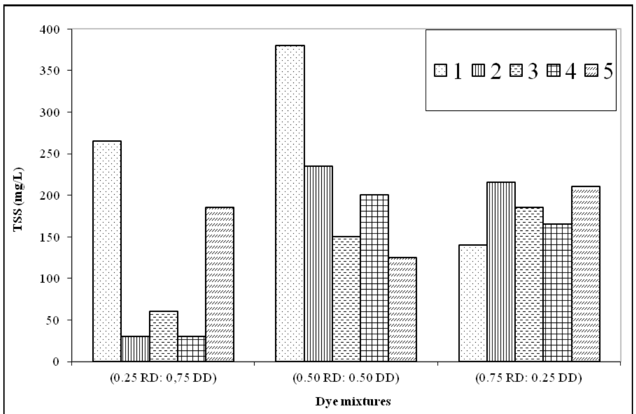

Fig. 5c: TSS.

Fig. 5: Treatment efficiency of mixed dye wastewater.

Fig. 5c shows the sludge production for the 3 different ratios of dye mixtures. Amount of sludge produced was measured by total suspended solids (TSS). For (RD:DD) = (0.25:0.75), TSS measured was within the range 30-265 mg/L, for (RD:DD) = (0.50:0.50) from 125-380 mg/L and for (RD:DD) = (0.75:0.25) amount of sludge produced was found to be within 140-215 mg/L. The amount of sludge produced using this system was considerably lower as compared to the Fenton oxidation and the coagulation using $FeCl_3$ as reported by Liu et al who performed treatment of a direct dye, a vat dye and an acidic dye using Fenton oxidation and coagulation using $FeCl_3$ (Liu et al. 2007). Sludge produced by Fenton oxidation was within 129 mg/L-546 mg/L, and coagulation with $FeCl_3$ within 326 mg/L-530 mg/L (Liu et al. 2007).

CONCLUSION

Experimental design was used as a statistical tool in evaluating the effect of factors and to further optimize treatment efficiency of a 1 g/L dye mixture containing a reactive (RD) and a disperse dye (DD) in the ratio of (RD:DD) = (0.25:0.75), (0.50:0.50), and (0.75:0.25) using H_2O_2/pyridine/Cu(II) system. The effect of pH was found to be not significant in this study while other factors such as [H_2O_2], [pyridine] and [Cu (II)] affect the treatment efficiency. For (RD:DD = 0.25:0.75), at the optimal concentration of 0.002 M H_2O_2, 0.066 M pyridine, and 0.0018 M Cu (II), the percentage of COD reduction was 87%, decolourization was found to be at 97%, and the amount of sludge produced was 185 mg/L. For (RD:DD = 0.50:0.50), at the optimal concentration of 0.024 M H_2O_2, 0.074 M pyridine, 0.0187 M Cu(II), the percentage of COD reduction was recorded at 86%, decolourization at 98%, and 125 mg/L sludge was produced. For (RD:DD = 0.75:0.25), at the optimal concentration of 0.004 M H_2O_2, 0.050 M pyridine, 0.0186 M Cu(II), percentage of COD reduction was 81%, decolourization was recorded at 96%, and sludge produced was 210 mg/L.

ACKNOWLEDGMENT

The authors would like to acknowledge the financial support provided by Universiti Kebangsaan Malaysia through Geran Universiti Penyelidikan (GUP-2014-034) and Dana Impak Perdana (DIP-2015-008).

REFERENCES

APHA, AWWA and WEF. 2005. Standard Methods for the Examination of Water and Wastewater. Washington, DC: American Public Health Association.

Baldrian, P., Merhautouá, V., Ntougias, S., Ehaliotis, C. and Nerud, F. 2006. The use of hydroxyl-radical-generating systems for the treatment of olive mill wastewaters. Folia Microbiol., 51(4): 337 -341.

Bali, U. and Karagözoglu, B. 2007a. Performance comparison of Fenton process, ferric coagulation and H_2O_2/pyridine/Cu(II) system for decolorization of Remazol-Turquoise Blue G-133. Dyes Pigments, 74: 73-80.

Bali, U. and Karagözoglu, B. 2007b. Decolorization of Remazol-Turquoise Blue G-133 and other dyes by Cu/pyridine/H_2O_2 system. Dyes Pigments, 73: 133-140.

Behnajady, M.A., Modirshahla, N. and Ghanbary, F. 2007. A kinetic model for the decolorization of C. I. Acid Yellow 23 by Fenton process. J. Haz. Mat., 148: 98-102.

Fathima, N.N., Aravindhan, R., Rao, J.R. and Nair, B.U. 2008. Dye house wastewater treatment through advanced oxidation process using Cu-exchanged Y zeolite: A heterogeneous catalytic approach. Chemosphere, 70: 1146-1151.

Kim, T.H., Park, C., Shin, E.B. and Kim, S. 2004. Decolorization of disperse and reactive dye solutions using ferric chloride. Desalination, 161: 49-58.

Lee, K.E., Morad, N., Teng, T.T. and Poh, B.T. 2012. Factorial experimental design for reactive dye flocculation using inorganic-organic composite polymer. APCBEE P., 1: 59-65.

Lee, K.E., Morad, N., Teng, T.T. and Poh, B.T. 2014. Reactive dye removal using inorganic-organic composite material: kinetics, mechanism, and optimization. J. Disper. Sci. Technol., 35: 1557-1570.

Lee, K.E., Hanafiah, M.M., Halim, A.A. and Mahmud, M.H. 2015. Primary treatment of dye wastewater using aloe vera-aided aluminium and magnesium hybrid coagulants. P. Env. Sci., 30: 56-61.

Lin, S.H. and Lin, C.M. 1993. Treatment of textile waste effluents by ozonation and chemical coagulation. Water Res., 27(12): 1743-1748.

Liu, R., Chiu, H.M., Shiau, C.S., Yeh, Ruth Y.L. and Hung, Y.T. 2007. Degradation and sludge production of textile dyes by Fenton and photo-Fenton processes Dyes Pigments, 73: 1-6.

Montgomery, D. C. 2001. Design and Analysis of Experiments, 5th ed. New York: JohnWiley & Sons.

Neamtu, M., Yediler, A., Siminiceanu, I., Macoveanu, M. and Kettrup, A. 2004. Decolorization of disperse red 354 azo dye in water by several oxidation processes-a comparative study. Dyes Pigments, 60: 61-68.

Nerud, F., Baldrian, P., Gabriel, J. and Ogbeifun, D. 2001. Decolorization of synthetic dyes by the Fenton Reagent and the Cu/pyridine/ H_2O_2 system. Chemosphere, 44: 957-961.

Pavan, F.A., Gushikem, Y., Mazzocato, A.C., Dias, S.L.P. and Lima, E.C. 2007. Statistical design of experiments as a tool for optimizing the batch conditions to methylene blue biosorption on yellow passion fruit and mandarin peel. Dyes Pigments, 72: 256-266.

Robbins, M.H. and Drago, R.S. 1997. Activation of hydrogen peroxide for oxidation by copper(II) complexes. J. Catal., 170: 295-303.

Secula, M.S., Suditu, G.D., Poulios, I., Cojocaru, C. and Cretescu, I. 2008. Response surface optimization of the photocatalytic decolorization of a simulated dyestuff effluent. Chem. Eng. J., 141: 18-26.

Sermin, G., Özlem, Ö. and Oktay, E. 2007. Ozonation of C.I. Reactive Red 194 and C.I. Reactive Yellow 145 in aqueous solution in the presence of granular activated carbon. Dyes Pigments, 75: 426-431.

Verma, P., Shah, V., Baldrian, P., Gabriel, J., Stopka, P., Trnka, T. and Nerud, F. 2004a. Decolorization of synthetic dyes using a copper complex with glucaric acid. Chemosphere, 54: 291-295.

Verma, P., Baldrian, P., Gabriel, J., Trnka, T. and Nerud, F. 2004b. Copper-ligand complex for the decolorization of synthetic dyes. Chemosphere, 57: 1207-1211.

Watanabe, T., Koller, K. and Messner, K. 1998. Copper-dependent depolymerization of lignin in presence of fungal metabolite, pyridine J. Biotechnol., 62: 221-230.